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3

Transport and Electro-optical Properties in Polymeric Self-assembled Systems

Olli Ikkala and Gerrit ten Brinke

3.1

Introduction

3.1.1

Background on Polymeric Self-assembly and Supramolecular Concepts

A central theme in materials science involves efforts to tune the properties of materials according to the requirements of the applications. This usually requires that several properties have to be tailored simultaneously and perhaps even synergistically, which can be nontrivial. For example, the electrical and mechanical properties typically have to be tailored simultaneously in combination with stability, processability and economics. Feasible combinations of polymeric properties have been widely pursued using multicomponent materials and here the controlled periodic nanoscale structures of block copolymers were appreciated at an early stage (e.g. [1–3]). Encouraged by the rapid development of supramolecular chemistry [4, 5], tailored physical interactions have recently been used to allow supramolecular polymers to be obtained [6–11]. Finding and tailoring new functionalities have become one of the main efforts and the biosciences have been a source of inspiration (e.g. [12–15]). Periodic nanoscale structures have been denoted differently depending on the background of the researchers. For example, in block copolymers, periodic nanostructures have been denoted microphase separation, nanophase separation, self-assembly, mesomorphism or self-organization. Shape-persistent mesomorphic groups, such as rigid rods, can also be incorporated to facilitate the structures and in such cases the terms mesomorphism or liquid crystallinity have typically been used [16–22]. Note that the definitions seem not to be strict; for example, the structure formation of aqueous surfactant systems has been denoted lyotropic liquid crystallinity (e.g. [23, 24]). Therefore, in this treatment, the term self-assembly is adopted. It has been discussed previously how nanoscale structures can result from competing attractive and repulsive interactions [25]. There the concept was denoted self-organization. In thermodynamics, however, self-organization some-

times refers to dissipative structure formation [26, 27] and self-assembly is preferred here. Therefore, in this chapter we understand by self-assembly spontaneous structure formation due to competing attractive and repulsive interactions in the fluid, glassy or crystalline state. Self-assembly can also be static and dynamic [28], and numerous examples have been presented in this and closely related fields (e.g. [19–22, 28–47]).

As mentioned, a classical example of polymeric self-assembly is provided by block copolymers [1, 2, 40, 41, 48–52]. As most polymers do not mix, they are mutually repulsive, taken that the chains are sufficiently long. If they are covalently connected within the same molecules to form block copolymers, i.e. connected by infinite attractive interaction, the free energy is minimized upon forming nanoscale structures. The structures depend on the chemical nature of the blocks and also on the temperature (which are combined within the χ -parameters), the length of the blocks, the architecture and the number and sequence of the blocks. There can be two, three or more repulsive blocks and they can be connected to form different architectures, such as linear, comb-shaped, star-shaped (microarm), T-shaped, H-shaped, (hyper)branched or dendritic shapes. The blocks can be flexible, forming coiled conformations, semi-rigid or even completely rod-like, which are prone to mutual aggregation. Figure 3.1 shows some examples of different block architectures. If there are two flexible chains connected in a linear fashion as in a classical diblock copolymer, spherical, cylindrical, lamellar and gyroid and hexagonal perforated structures are obtained (Fig. 3.2). The disordered phase prevails at very high temperatures and there can be a sequence of different phases as a function of temperature. If the

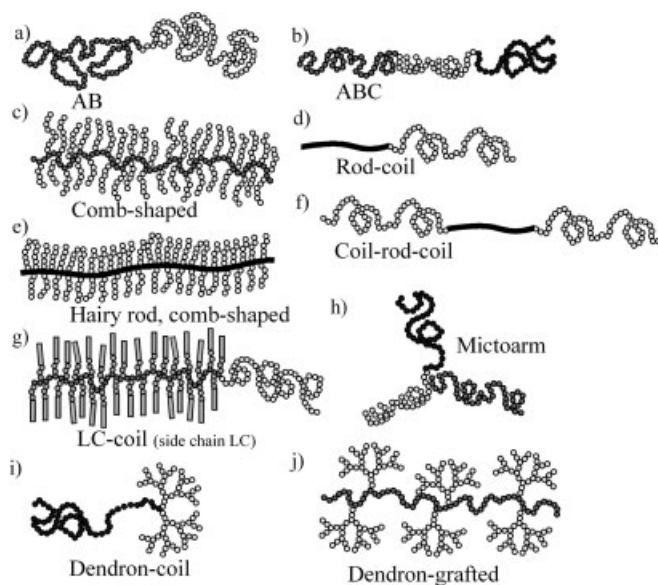


Fig. 3.1 Examples of different block copolymer architectures.

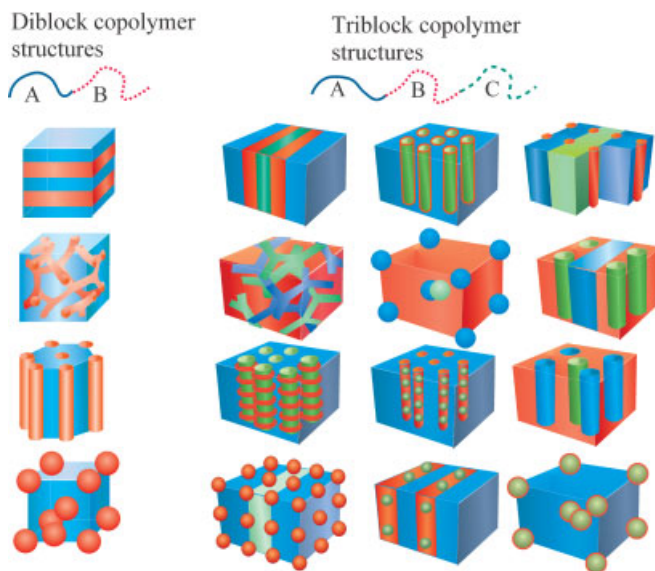


Fig. 3.2 Examples of self-assembled AB diblock copolymer and ABC triblock copolymer structures obtained by connecting flexible polymer chains in a linear architecture. Adapted from [49].

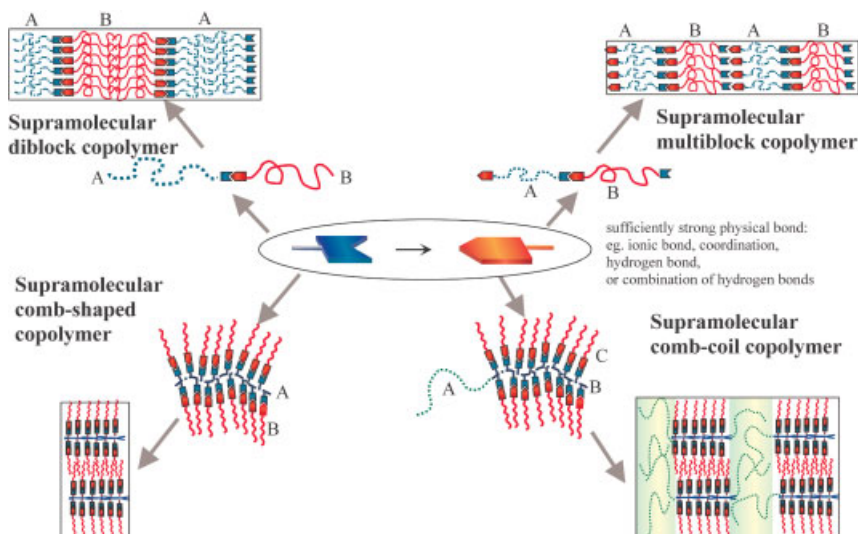


Fig. 3.3 Some examples of various architectures for self-assembly using supramolecular interactions.

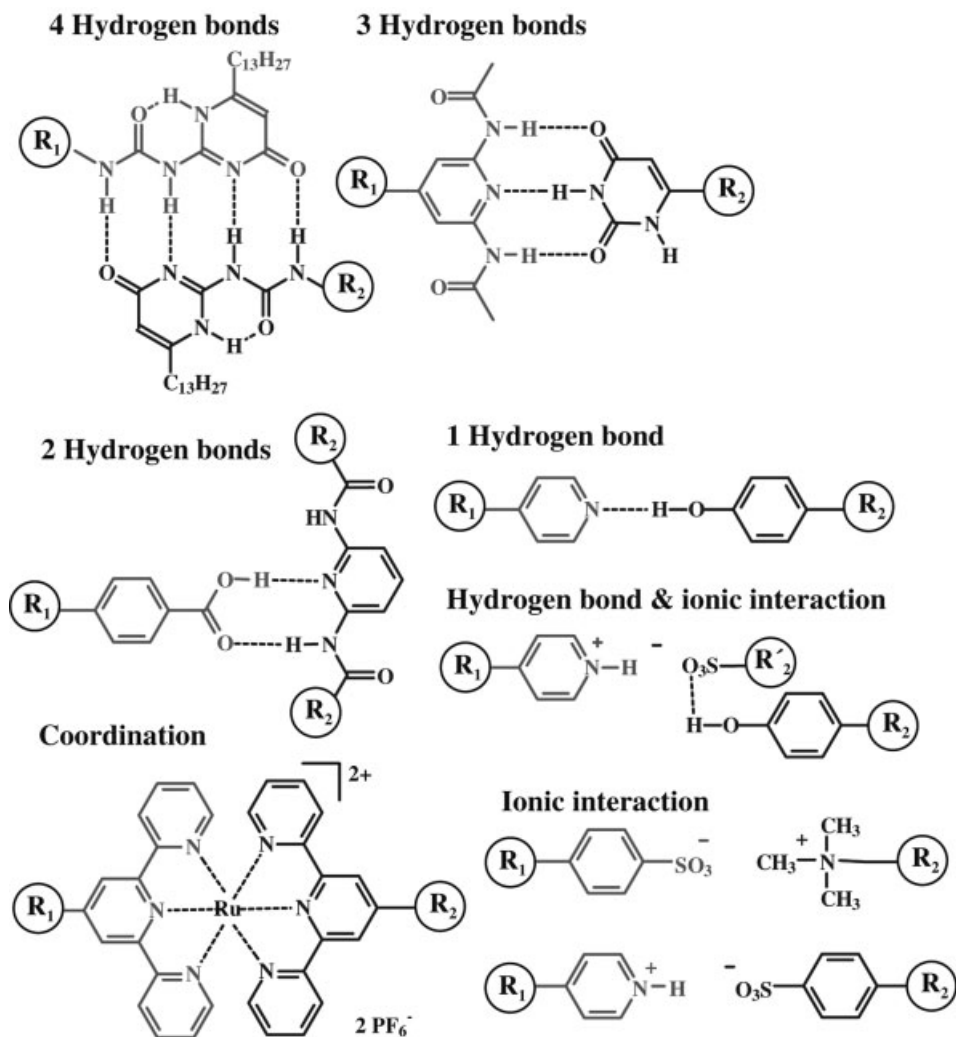


Fig. 3.4 Selected examples of the use of physical interactions to construct self-assembling materials (see also Fig. 3.3) [4, 6, 7, 11, 21, 34, 44, 47, 74, 92, 96]. R_1 and R_2 represent the repulsive moieties to be connected to achieve self-assembly.

number of the blocks is increased to three, more structures are available, for example core-shell cylinders (Fig. 3.2). Further increase in the number of blocks leads to a rapidly increasing number of structures and structural complexity.

Another aspect has become relevant due to supramolecular chemistry [4, 5], i.e. that the attractive interactions can also be physical interactions, taken that they are sufficiently strong to withstand the repulsive interactions between the

blocks. The interactions can be ionic [43, 53–66], in which case the term ionic self-assembly can be used [42]; they can be hydrogen bonds or their combinations [10, 11, 21, 22, 34, 67–88]; they can be coordinative [89–93]; or they can in principle be any sufficiently strong attractive interaction or their combination. Over the years, several examples have arisen of physical interactions that enable one to prepare polymer-like materials (Figs. 3.3 and 3.4). For example, ionically interacting sites at the ends of telechelic polystyrene and poly(ethylene oxide) form “ionic multiblock copolymers” [55], the combination of four hydrogen bonds leads to linear polymeric supramolecules [6, 10, 11] where self-assembly can be achieved [94] and coordination bonds can be used to prepare polymers [7, 8, 95] and “coordinative block copolymers” [91, 92].

3.1.2

General Remarks on Polymeric Self-assembly in Relation to Electrical and Optical Properties

This chapter emphasizes selected aspects of tuning the electric and optical functionalities using polymeric self-assembly in the light of selected recent work. Protonic and ionic transport using self-assembled polymers will be discussed first, as they could have relevant applications in energy storage applications, i.e. proton conductors for fuel cell membranes [97] and the Li^+ conductors [98, 99] for batteries, where the aim is to combine high protonic or ion transport with sufficient mechanical properties and stability. Undoped conjugated polymers are semiconducting, they can be doped for conductivity and they have interesting electrical and optical properties [47, 100–102]. Due to the rigidity of the conjugated chains, there is a tendency for aggregation, which can lead to infusibility and poor solubility. Incorporating side-chains improves these aspects (see Fig. 3.1), but simultaneously due to the side-chains they typically also self-assemble. Therefore, self-assembly is intimately but indirectly connected to many of the conjugated polymers.

In general, the electrically conducting multicomponent materials require continuous pathways of conducting channels across the material, i.e. percolative systems. This is a demanding requirement, as self-assembly typically leads only to local order and macroscopically the materials are usually constituted of domains with differently aligned self-assembled domains and domain boundaries between them. Notably, the electrically conducting channels can be discontinuous at the domain boundaries. More generally, aligned and monodomain structures in block copolymers have been pursued using several concepts, for example using thin films where the surface energies play a major role, electric fields, magnetic fields, flow alignment and graphoepitaxy [86, 103–122]. Therefore, in many of the applications requiring enhanced electrical transport, a generic goal in relation to self-assembly is to prepare monodomain structures having e.g. well-aligned cylindrical or lamellar conducting channels or monodomain co-continuous phases, such as the gyroid structure or other networks. Another scheme is to aim at molecular reinforcement due to self-assembly, in which case the

matrix is conducting and the material contains self-assembled reinforcements. Still another possibility is to use (polymeric) colloids, typically spheres, and to tune the conductive percolative channels using self-assembly. Finally, one should emphasize the different ways of achieving continuous networks within polymeric matrices using block copolymers and self-assembling moieties [52, 123–127].

In relation to the optical properties, self-assembly can allow a variety of different properties, for example photonic bandgap materials (or dielectric mirrors), materials for photovoltaics, nonlinear optics, polymeric light-emitting devices, optical storage and sensors and photorefractive materials. Some of them are discussed here in the perspective of polymeric self-assembly.

A final remark is that due to the broad field, all facets of this rapidly developing field cannot be covered within the present limited space. In particular, we do not deal with layer-by-layer and self-assembled monolayer techniques, Langmuir–Blodgett techniques, electrochromic and photorefractive materials, and electroluminant polymers are mentioned only in passing.

3.2

Transport of Ions and Protons within Self-assembled Polymer Systems

3.2.1

Self-assembled Protonically Conducting Polymers

Proton conductivity or proton transport is of major interest in several fields, ranging from biological systems to materials science combining chemistry and physics, some of them having important technological potential, for example in fuel cells (for the extensive literature on various applications see for example [128–156] and more generally for ion-containing polymers [157]). Responsive smart materials will also be presented, illustrating possibilities offered by phase transitions to tune the properties.

There are several stringent requirements for the fuel cell membrane material between the anode and the cathode: the material should be highly protonically conducting but still not electronically conducting, should be mechanically strong to withstand robust use and should withstand harsh chemical environments and the economics should be acceptable. To add one further requirement: the feasible operating temperature can be in excess of 100°C, where the possible detrimental effects of CO on the catalytic materials are reduced, depending on the fuel cell concept and materials used.

Widely studied protonically conducting materials are polymeric perfluorosulfonic acids which contain fluorocarbon chains and where sulfonic acid groups are grafted on the side-chains [158]. It becomes conducting as the sulfonic acids are highly hygroscopic and the polymer can be considered as a percolating medium for water-mediated proton conductivity. Water has been the most studied proton conducting medium [130, 159]. Protonated water species, such as H_3O^+

and H_5O_2^+ , can diffuse, which is called the vehicular mechanism. On the other hand, water molecules form hydrogen-bonded networks as they are both hydrogen bonding acceptors and hydrogen-bonding donors. In such a medium, proton hopping from the protonated water species to nonprotonated H_2O species can take place, followed by their reorientation, i.e. the Grotthuss mechanism [130, 159]. In order to exhibit substantial conductivity across the membrane, the water clusters have to form connected networks, i.e. they have to percolate. This requires that during the operational conditions, there has to be a sufficient level of moisture to allow water absorption and the connectivity of the protonically conducting channels should be controllable and stable. The latter aspect has been the subject of intense study in perfluorinated membranes already for an extended period [146, 158].

If the optimal operating temperature is high, water is not a preferred protonically conducting medium due to its low boiling-point. There has been an intense search for alternative amphoteric hydrogen-bonded compounds capable of rendering high proton conductivity. Phosphoric acid, pyrazole, imidazole and benzimidazole have been studied [143, 149, 160–162]. Phosphoric acid is relatively highly conducting [163]. It, and other acids, have been blended with poly(ethylene oxide), poly(vinyl alcohol), polyacrylamide and basic polymers rendering salts, such as polyethylenimine, polydiallyldimethylammonium salts, poly(4-vinylimidazole), poly(4-vinylpyridine) and polybenzimidazole [164–175]. The acid–base complexes have aroused interest even in the anhydrous case [176]. Another concept has been based on imidazoles and it has also been immobilized using polysiloxane backbones to which imidazoles are connected using flexible oligoethylene spacers [161]. To enhance transport, one may favor systems with low proton density and a large number of binding sites [131].

Methods to achieve conducting domains based on self-assembly are addressed next. Undecylimidazole protonated by a small amount of monododecylphosphoric acid leads to lamellar self-assembly and conductivity under anhydrous conditions [177]. Extending to polymers, there are several challenges: A narrow polydispersity is required to control the structures. This typically requires living polymerization, which may not be straightforward using polymers with the chemical stability required in fuel cells. Second, self-assembly renders only local structures and it is nontrivial to achieve continuous conducting channels across the membrane. An elegant approach could be to construct a gyroid structure (Fig. 3.2) but it may be nontrivial to achieve in large-scale applications even using more straightforward materials. Another scheme would be to use a cylindrical structure with the cylinders aligned across the membranes.

There have been extensive studies on block copolymers consisting of polyolefinic and polystyrene blocks where the latter blocks are partially sulfonated for enhanced water absorption and protonic conductivity (e.g. [178–201]). Typical materials are hydrogenated triblock copolymers, such as polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS), polystyrene-*b*-polyisobutene-*b*-polystyrene (SIBS) and polystyrene-*b*-polyethylene/butene-*b*-polystyrene (SEBS), and also architectures other than linear have been used (Fig. 3.5). Taking SEBS with 28% polystyrene,

where the polystyrene is partially sulfonated, a well-defined lamellar self-assembly is obtained on casting the membrane from THF [186, 198]. However, the conductivity across the membrane, i.e. across the lamellae, remains rather low, which is not surprising, as the lamellae tend to be aligned along the external surfaces [186, 198]. Methanol and water swelling change the morphology to a more disordered co-continuous-like structure and the conductivity increases across the membrane. However, the methanol transport also increases which is undesirable. The structures and conductivity can be tuned by changing the degree of sulfonation [185, 188] and the methanol permeation can be reduced [188] by chemical modifications using maleic anhydride groups within the ethylene/butene midblocks. Sulfonated SBS in combination with UV cross-linked butene groups has been used to immobilize the cylindrical protonically conducting sulfonated PS domains [189]. The conductivity is comparable to that of Nafion and the methanol permeability is strongly reduced [189]. A systematic study dealing the correlation between the structure and conductivity was recently reported using sulfonated SIBS [195, 201] using a range of degrees of sulfonations and different solvents to cast the membranes. Well-defined cylindrical and lamellar self-assembled ion channels could be obtained but typically they are parallel to membrane surfaces, leading to reduced conductivity across the mem-

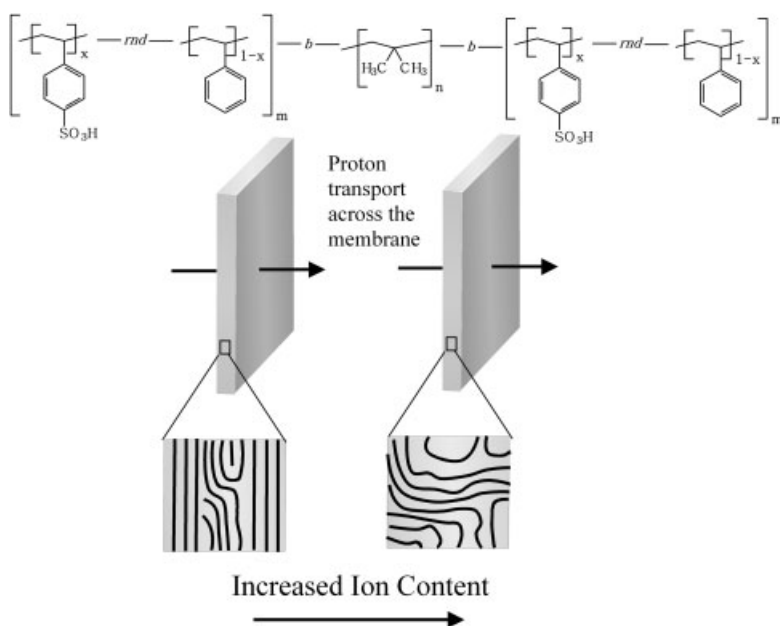


Fig. 3.5 Sulfonated polystyrene-*b*-polyisobutene-*b*-polystyrene leads to well defined self-assembled structures at low levels of sulfonation and the domains are aligned parallel to the membrane. Increasing the sulfonation level leads to less periodic structures but also to increased proton transport [201].

brane. At higher ion contents, the structures become less well defined, but the conductivity across the membranes increases substantially. Such sulfonated tri-block copolymers can render conductivity values approaching those of Nafion, but the methanol transport and chemical stability may still limit the practical use in fuel cells.

Another effort to control the structure of the conducting sulfonated polystyrene domains is based on the polystyrene backbone, where well-defined polystyrene sulfonate grafts are connected using controlled spacings (Fig. 3.6) [202]. This leads to 5–10-nm wide sulfonated polystyrene channels through the polystyrene matrix which are connected as a continuous ionic network, thus providing conductivity 0.24 S cm^{-1} with a styrene sulfonic acid loading of 19.1 mol% and which contains only 37 vol.% water. This conductivity is 3–5 times larger than that of Nafion 117 for a similar water content.

The conducting channel orientation and connectivity are critical for high conductivity. It is nontrivial to obtain perpendicular self-assembled structures across block copolymer films and this requires careful consideration of solvents, surface energies, film thicknesses, nanoparticles and potentially using an external field [112–117, 122, 203–206]. That aligned protonically conducting self-assembled structures can lead to anisotropic transport has been separately investigated [87, 175, 195, 207]. A model material related to fuel cells is polystyrene-*b*-poly(4-vinylpyridine) mixed with phosphoric acid, where a lamellar self-assembly was obtained having alternating lamellar domains of polystyrene and an acid-base mixture of P4VP and phosphoric acid [175]. The pure P4VP(H_3PO_4) $_x$ is relatively well conducting, i.e. $10^{-2} \text{ S cm}^{-1}$ at 100°C for $x=2.5$. The lamellar self-assembled structures were flow aligned and the alternating conducting and PS lamellae are both parallel to the flow after the alignment. An anisotropy in the conductivity was observed, but the anisotropy was only one order of magnitude. This suggests that it may be challenging to have macroscopic nanoscale domains that do not have “dead-ends” even if the structures are aligned.

Another approach for well-defined alignment of self-assembled conducting domains is based on thin films where the interfacial energies of the external sur-

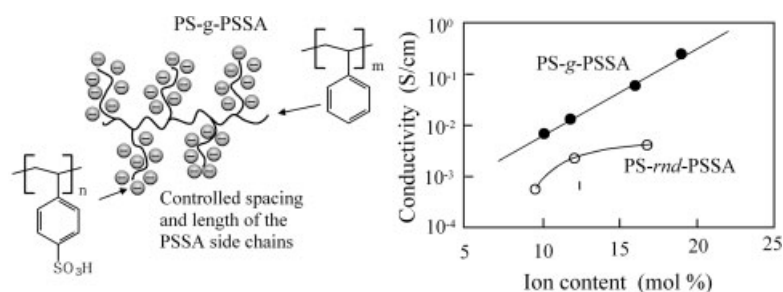


Fig. 3.6 A concept to achieve conducting hydrated ionic poly(styrenesulfonic acid) (PSSA) channels through a polystyrene (PS) matrix using grafting [202].

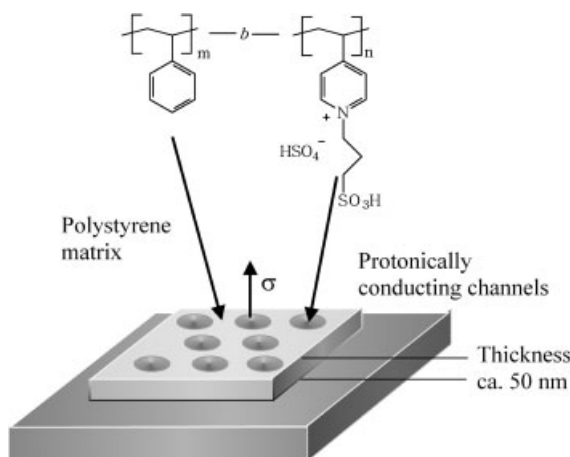


Fig. 3.7 Protonically conducting thin membrane, showing high conductivity anisotropy across the membrane [208].

faces can be used [204, 205]. To achieve self-assembled protonically conducting membranes, the pyridine groups of polystyrene-*b*-poly(4-vinylpyridine) were ionically functionalized, leading to cylindrically self-assembled ionic domains (Fig. 3.7) [208]. The resulting films show highly anisotropic conductivity, i.e. 0.015 S cm^{-1} across the membrane and very low conductivity $< 10^{-15} \text{ S cm}^{-1}$ to the lateral direction at 25°C under 45% relative humidity. We emphasize that the concept is based on the very thin films (50 nm) and, in fact, the aspect ratio of the channels is small in this case.

Chemically more stable materials are preferred for fuel cell membranes, such as fluorinated materials, but even aromatic polymers may suffice for less stringent applications [137, 151, 154, 209].

Recently there have been efforts to construct block copolymers based on fluorinated blocks, aiming to combine self-assembly and chemical stability. The proton conductivity of sulfonated polysulfones possessing a relatively low degree of sulfonation can be enhanced by block copolymerization with poly(vinylidene difluoride) (PVDF) [210]. This may be due to the self-assembly between the sulfonated and hydrophobic blocks. Sulfonated poly(aryl ether ketone) copolymers based on 4,4'-(hexafluoroisopropylidene)diphenol, 1,3-bis(4-fluorobenzoyl)benzene and disulfonated difluorobenzophenone have good thermal and oxidative stability [211]. Amphiphilic block copolymers comprising sulfonated poly(vinylidene difluoride-*co*-hexafluoropropylene)-*b*-polystyrene were synthesized having moderately low polydispersity index [212, 213]. Transmission electron microscopy studies suggested interconnected networks of ion channels, each 8–15 nm wide and the conductivity was of the same order as that of Nafion. The proton conductivities reach $> 3.3 \times 10^{-2} \text{ S cm}^{-1}$ at 80°C . The films show structure at two length scales based on X-ray scattering: the structure at a length scale of ap-

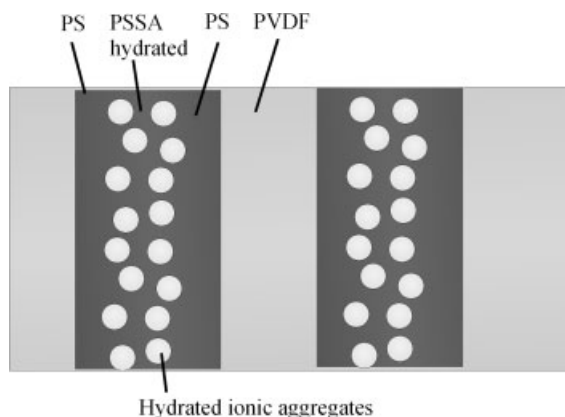


Fig. 3.8 Hierarchical self-assembly of protonically conducting poly(vinylidene difluoride-co-hexafluoropropylene)-*b*-polystyrene [213].

proximately 4 nm is due to the immiscibility of the polystyrene and the fluorinated blocks and a substructure within the sulfonated polystyrene domains exists due to segregation of the hydrated ionic groups and the hydrophobic polystyrene chains (Fig. 3.8). The longer length scale morphology shows relatively high ordering whereas within the sulfonated polystyrene blocks there is a more disordered structure.

A different concept for combining polymeric self-assembly and protonic conduction is based on colloidal self-assembly (Fig. 3.9) [214]. Lightly cross-linked ca. 500-nm polystyrene colloidal spheres were dispersed in ethanol with polystyrene-*b*-poly(2-vinylpyridine) block copolymer, which has a short polystyrene and a long poly(2-vinylpyridine) block. After solvent removal and under appropriate annealing, the colloidal system was deformed to polyhedra where the poly(2-vinylpyridine) surface layers percolate. Conductivity was obtained upon doping the latter using sulfonic acid [214]. The colloidal concept has been developed further to lead relatively high protonic conductivity [215].

Protonically conducting self-assembled polymers allow also smart and responsive materials. The pyridine groups of diblock copolymer polystyrene-*b*-poly(4-vinylpyridine), PS-*b*-P4VP were ionically complexed with methanesulfonic acid (MSA) and the resulting poly(4-vinylpyridinium methanesulfonate) was hydrogen bonded with an amphiphile, pentadecylphenol (PDP). The latter molecule consists of a nonpolar pentadecyl alkyl tail and a polar end-group, consisting of hydrogen-bonding phenol. This leads to hierarchical lamellar-*within*-lamellar self-assembly at two length scales: the first self-assembly between the PS and P4VP(MSA)(PDP)-block, leading to a periodicity of ca. 35 nm, and within the latter block another level of self-assembly with a periodicity of 4.8 nm takes place, where the PDP and P4VP(MSA) form alternating layers. A sequence of phase transitions takes place upon heating and cooling, which manifests in the

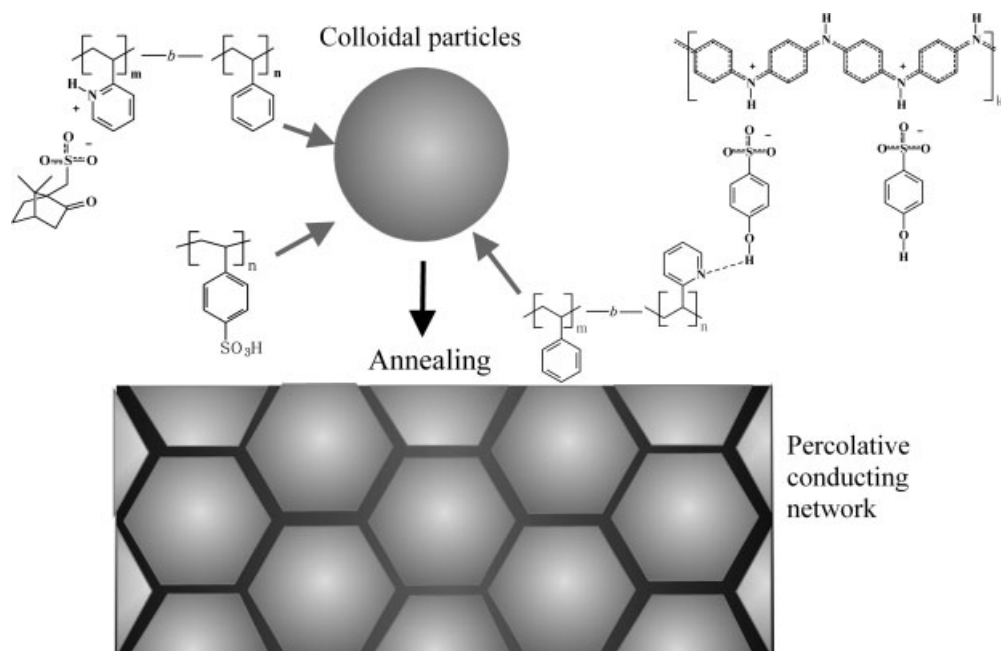


Fig. 3.9 Colloidal polymer spheres allow templating of protonically or conjugated polymers to allow percolated networks [214–216].

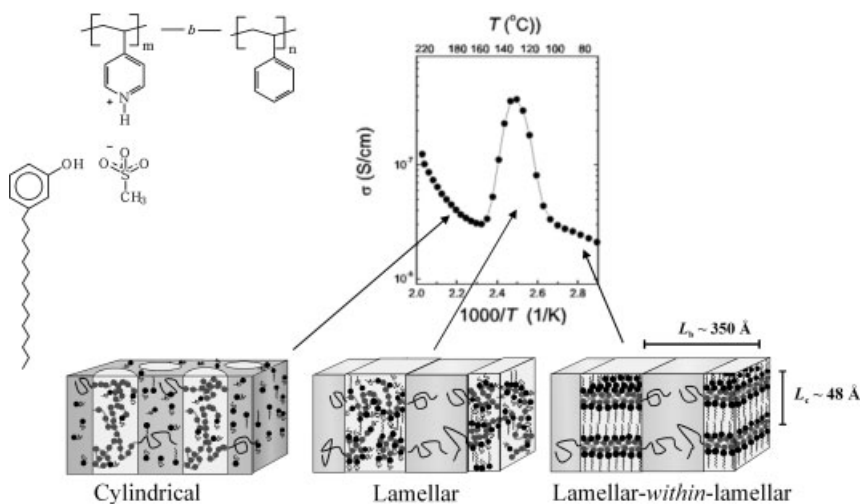


Fig. 3.10 Hierarchical self-assembly of polystyrene-*b*-poly(4-vinylpyridinium methanesulfonate) hydrogen bonded with pentadecylphenol amphiphile [34]. As a function of temperature different self-assembled phases are obtained, which consequently affects the conductivity.

conductivity (Fig. 3.10). More generally, related hierarchically self-assembled systems allow tuning of the properties by controlling the structures at different length scales [44, 87, 207, 217–222]. Polyelectrolyte–surfactant complexes self-assemble into various nanoscale structures and they can exhibit electrical conductivity [223, 224].

3.2.2

Self-assembled Ionically Conducting Polymers

Self-assembled ionic conductors have recently been reviewed [21, 22, 225]. Ionic conductors are required in various electrochemical applications based on polymeric electrolytes, especially for Li^+ batteries [98, 226–231]. A widely studied system is a salt-in-polymer system where a lithium salt, e.g. $\text{CF}_3\text{SO}_3\text{Li}$, has been solvated in the poly(ethylene oxide) (PEO) matrix to form solid polymer electrolytes [98, 231–236]. However, enhanced ionic conductivity requires high chain mobility and at room temperature the conductivity can be reduced due to crystallization of PEO. To allow amorphous materials with low glass transition temperatures has been tackled in many ways, e.g. using plasticizers or using short PEO chains that have increased mobility and suppressed crystallization where the graft and branched architectures have been useful [237–240]. Also, self-assembly is used where amorphous ethylene oxide-containing domains are incorporated within block copolymeric structures, leading to synergistic properties [225, 241–243].

There were early efforts to combine PEO within block copolymer structures, for example by grafting short PEO grafts to the middle block of polystyrene-*b*-polybutadiene-*b*-polystyrene triblock copolymer [244, 245]. Upon solvating $\text{CF}_3\text{SO}_3\text{Li}$ to the PEO, conductivity in the order of $10^{-5} \text{ S cm}^{-1}$ at ambient temperature was obtained and self-assembly and suppressed PEO crystallization were observed. Polystyrene-*b*-polyhydroxystyrene-*b*-polystyrene with PEO grafts within the middle block showed self-assembly and relatively high ionic conductivity upon solubilizing LiClO_4 in the PEO grafts [246]. Polyethylene-*b*-poly(ethylene oxide-*co*-propylene oxide)-*b*-polyethylene triblock copolymers with 10 wt.% of the end blocks leads to gelation based on physical networking [247]. Lithium bis(trifluoromethylsulfonyl)imide salt (LiTFSI) was solvated therein to allow conductivity approaching $10^{-5} \text{ S cm}^{-1}$ at 20°C [247, 248]. A comb-shaped architecture of gel electrolyte consists of a polystyrene backbone where PEO or poly(ethylene oxide-*co*-propylene oxide) chains are connected [249]. All the polyether side-chains were terminated by hydrocarbon (C_{16}) chain ends. LiTFSI salt solvation leads to ion conductivity that reached $10^{-2} \text{ S cm}^{-1}$ at 20°C . A related approach is based on amphiphilic methacrylate polymers with oligo(ethylene oxide) segments terminated by a linear alkyl chain [250]. The polymers self-assemble into nanometer-thick lamellar structures with alternating layers of conductive ethylene oxide and insulating alkyl layers.

In an effort to combine rubbery mechanical macroscopic properties and self-assembled ionically conducting domains, poly(lauryl methacrylate)-*b*-poly[oli-

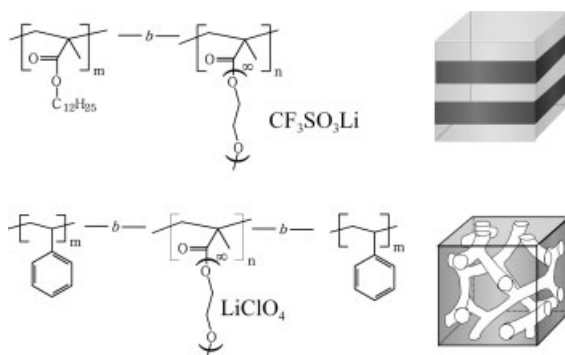


Fig. 3.11 Examples of self-assembled Li-conducting polymer electrolytes [242, 251].

go(oxyethylene) methacrylate] diblock copolymers containing $\text{CF}_3\text{SO}_3\text{Li}$ were studied using different molecular weights and relatively narrow molecular weight distributions (Fig. 3.11) [241]. Reducing the length of the lauryl side-chain to be only methyl, i.e. using poly(methyl methacrylate)-*b*-poly[oligo(oxyethylene) methacrylate], reduces the repulsion between the blocks and self-assembly does not occur [242]. However, adding $\text{CF}_3\text{SO}_3\text{Li}$ leads to self-assembly and conductivity. Therefore, both the structure and conductivity can be tuned by solvating the salt. Single-ion conducting block copolymer electrolytes were prepared using poly(lauryl methacrylate)-*b*-poly(lithium methacrylate)-*b*-poly[(oxyethylene)₉ methacrylate], in which case the counterions for lithium ions were bound to the polymer backbone [243]. This allows a lithium transfer number of unity and a conductivity of $10^{-5} \text{ S cm}^{-1}$ at 70°C . Various further modifications have recently been reviewed [225]. An effort to use the gyroid phase for Li^+ conductors was described using polystyrene-*b*-polyethylene oxide and LiClO_4 [251]. The conductivity level is relatively high, i.e. more than $10^{-4} \text{ S cm}^{-1}$ at room temperature. The polystyrene domains promote mechanical strength and the PEO domains allow ion conduction in the polymer electrolyte without any plasticizer.

The phase transitions of the self-assembled structures can have a major effect on the ionic conductivity, as in the case of protonically conducting self-assemblies [34]. A diblock copolymer was synthesized having a linear PEO block and dendron-like block with a controlled number and length of alkyl chains (Fig. 3.12) [252]. $\text{CF}_3\text{SO}_3\text{Li}$ was solvated in PEO. Such amphiphilic dendrons showed complex sequences of self-assembled phases ranging from crystalline lamellar, through cubic micellar ($Pm3n$), hexagonal columnar and continuous cubic ($Ia3d$) to fluid lamellar mesophases, until a disordered structure, each having their characteristic conductivity.

Extensive research has been carried out to achieve a helical PEO-like environment for the Li^+ ions and to combine it with self-assembly [236, 253–259]. The building blocks are poly[2,5,8,11,14-pentaoxapentadecamethylene(5-alkyloxy-1,3-phenylene)] chains, which typically have hexadecylmethylene (C_{16}) side-chains (Fig. 3.13). Due to the comb-shaped architecture consisting of the backbone and

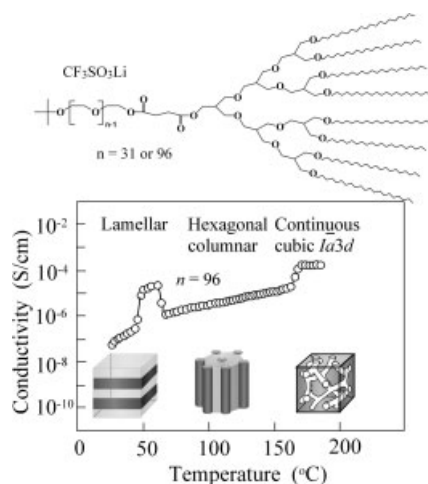


Fig. 3.12 An example of dendron-containing block copolymers and the observed ionic conductivity as a function of temperature upon mixing with $\text{CF}_3\text{SO}_3\text{Li}$ [252].

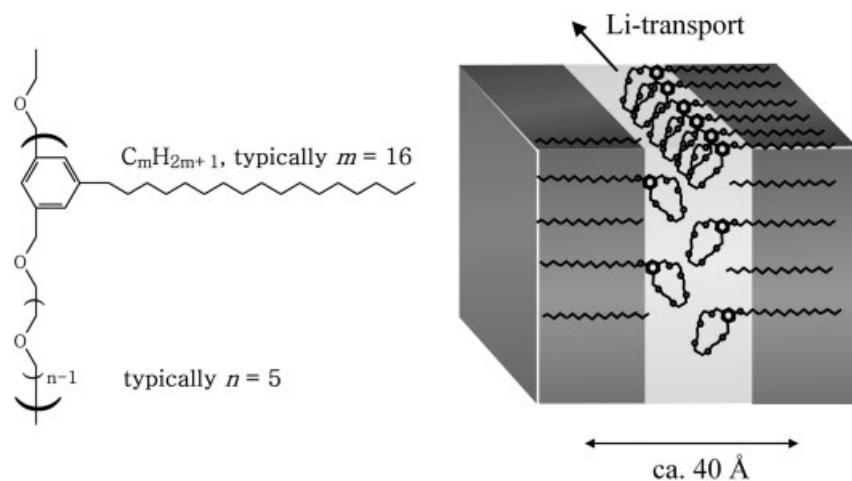


Fig. 3.13 Self-assembled Li^+ conductors consisting of poly[2,5,8,11,14-pentaoxapentadecamethylene(5-alkoxy-1,3-phenylene)] [236, 253–259].

the repulsive dense set of side-chains, lamellar self-assembly is achieved where the alkyl chains interdigitate. The polymer backbone forms helices which incorporate the Li^+ ions. The compositions may also include additional polymer components or alkanes to tune the properties. The conductivity levels are in excess of $10^{-4} \text{ S cm}^{-1}$ at 40°C , where additional alkyl groups can be useful within the alkyl tail domains. A copolymer was also synthesized based on poly[2,5,8,11,14-pentaoxapentadecamethylene-(5-alkoxy-1,3-phenylene)] and poly[2-oxatrimethylene(5-alkoxy-1,3-phenylene)], where the alkyl side-chains are hexadecyl or mixed dodecyl–octadecyl (50:50) [260]. A conduction mechanism is proposed

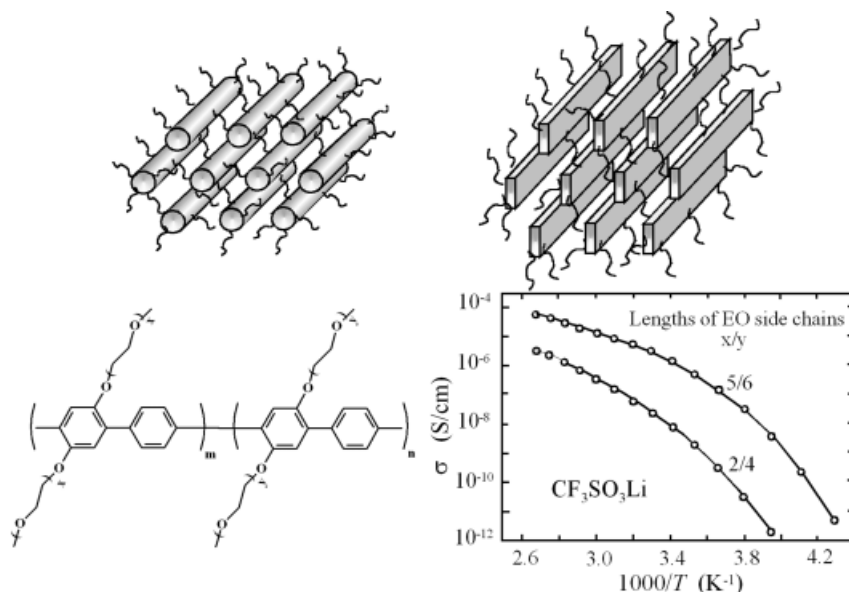


Fig. 3.14 If poly(*p*-phenylene) is grafted with a dense set of side-chains, lamellar or cylindrical self-assemblies can be obtained [264]. Poly(*p*-phenylene) containing two different lengths of ethylene oxide side-chains and the resulting ionic conductivity values obtained upon mixing CF₃SO₃Li for side-chains of lengths 5 and 6 ethylene oxide repeat units [266].

whereby Li⁺ hopping takes place along rows of decoupled aggregates (dimers/quadrupoles).

It can be challenging to ensure the alignment and connectivity of the ionically conducting self-assembled domains within a matrix polymer. This encourages the study of another route where the ionically conducting polyelectrolyte phase is molecularly reinforced using self-assembled rigid rod polymers. One concept is based on grafting short ethylene oxide chains to a rigid rod poly(*p*-phenylene) (PPP) polymeric backbone (Fig. 3.14). Unfunctionalized PPP is not soluble and does not melt. However, incorporating a dense set of side-chains leads to “hairy rods” [261–263], i.e. a comb-shaped architecture, where the mutual aggregation of the rods is reduced by the side-chain spacers [264, 265]. By using a statistical copolymer PPP(EO)_{x/y} involving two different side-chain lengths (*x* and *y*) of oligo(ethylene oxide) side-chains, self-assembled materials have been introduced where the tendency for the side-chain crystallization is suppressed. Li⁺ conduction is achieved by adding LiTFSi [266]. For longer side-chains, consisting of e.g. *x*=5 and *y*=6 ethylene oxide repeat units, the materials exhibit an order–disorder transition (in the range 90–160 °C) to a disordered isotropic state upon heating. If the side-chains are shorter, e.g. *x*=4 and *y*=2, the lamellar structure prevails up to 240 °C. In another version, the anionic counterions have been incorporated within the polymeric backbone [267].

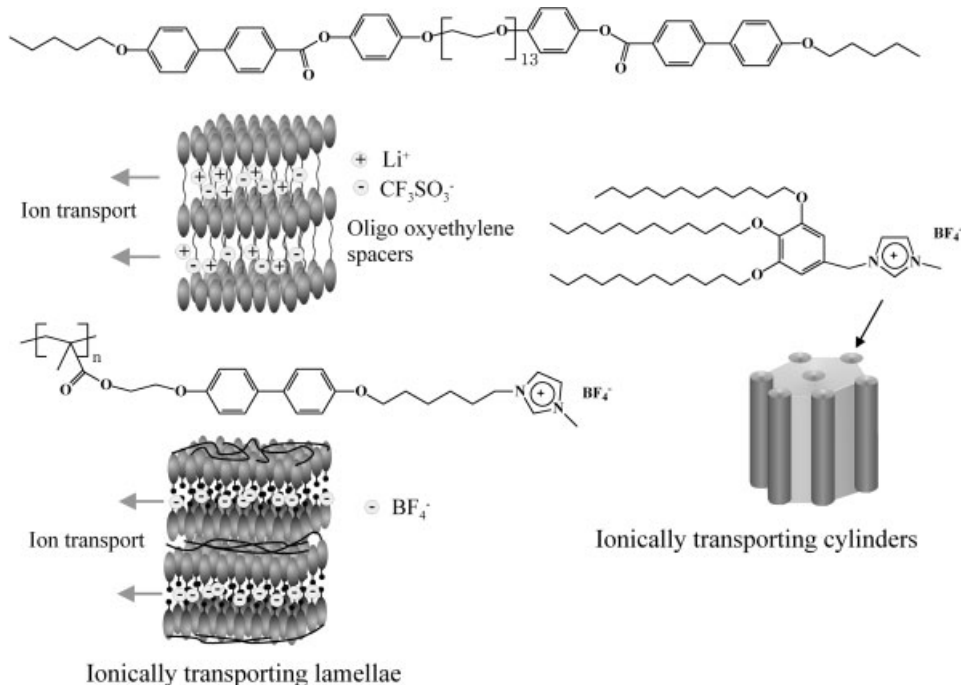


Fig. 3.15 Examples of concepts to control the dimensionality of ionic conductivity [21, 268–270].

Mesogenic groups are versatile for controlling self-assembly when various functionalities and anisotropic properties are pursued; for a recent review, see [22]. Mesomorphic dimeric compounds consisting of rigid mesogenic cores and flexible oxyethylene chains are able to complex $\text{CF}_3\text{SO}_3\text{Li}$ to form a lamellar smectic self-assembly (Fig. 3.15) [268]. The ionic conductivity is anisotropic and reaches $5.5 \times 10^{-4} \text{ S cm}^{-1}$ parallel to the layers. By tailoring the chemical structure of the self-assembling groups, it is possible rationally to design the dimensionality of the conductivity [21]. One can also connect the structure-directing mesogens as side-chains of polymers to allow lamellar ion conducting layers (Fig. 3.15) [269].

3.3

Self-assembly of Conjugated Polymers

There is a recent and comprehensive review [47] on various aspects of self-assembled and supramolecular conjugated systems and in this discussion only a few of the concepts are dealt with. Conjugated polymers have either a totally rigid rod-like conformation or a semi-rigid coiled conformation and they typically include aromatic or heteroaromatic groups capable of π -stacking [100]. There-

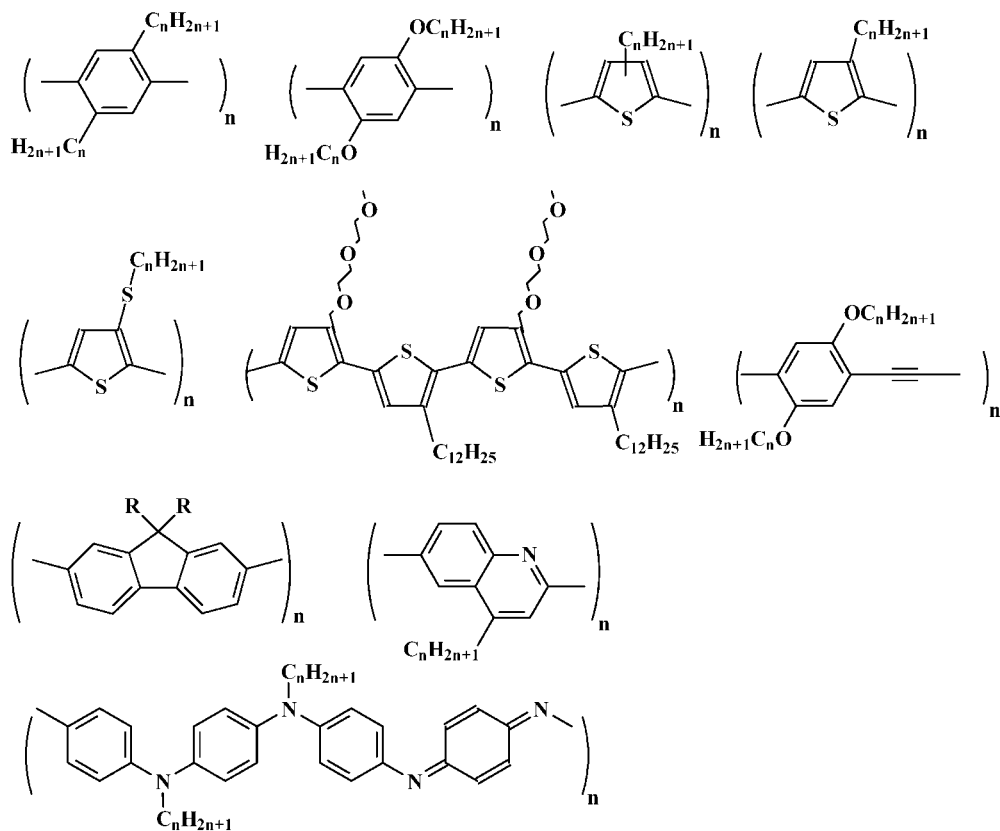


Fig. 3.16 Examples of hairy rod polymers consisting of conjugated polymers with covalently bonded flexible side-chains. The backbones consist of poly(*p*-phenylene)s, polythiophenes, poly(phenylene vinylene)s, polyfluorenes, polyquinolines and polyanilines.

fore, they are prone to aggregation and it is not surprising that in the general case they do not melt and they can be poorly soluble in common solvents. The aggregation can be controlled by incorporating proper side-chains to the conjugated backbone and such a comb-shaped architecture is also denoted “hairy rods” (Figs. 3.14 and 3.16) [262, 264–266, 271, 272]. The covalently bonded side-chains can also be regarded as “bound solvent molecules” and they also render surface activity towards another solvent phase. But additionally, the side-chains can lead to self-assembly as the flexible side-chains are repulsive [262, 273]. For example, poly(*p*-phenylene) (PPP) is an insoluble and infusible conjugated polymer. Several types of hairy rods have been prepared (Fig. 3.16) [262, 264–266, 274–277]. The polymers self-assemble to cylindrical or lamellar phases depending on the type and length of the alkyl chains [264, 266]. The nature and length

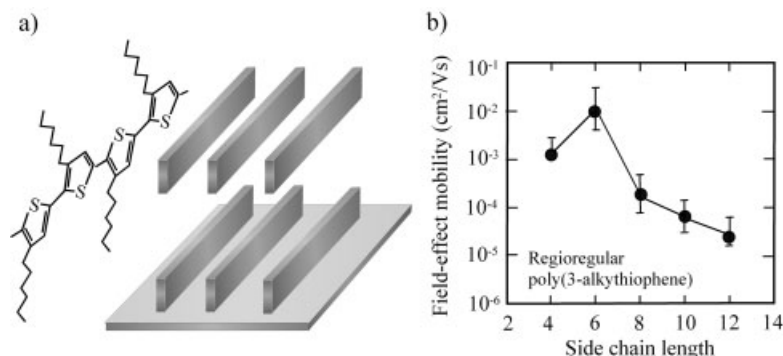


Fig. 3.17 (a) Lamellar self-assembly of regioregular poly(3-hexylthiophene) which leads to enhanced charge transport [301]. (b) Effect of side-chain length on hole mobility [299, 301].

of the covalently bonded side-chains have a large effect on the phase behavior [273].

Alkyl-substituted polythiophenes (Fig. 3.16) were first studied in the 1980s and the self-assembled lamellar structures in bulk were revealed using X-ray scattering [278–283]. For example, regiorandom poly(octylthiophene) shows a lamellar self-assembly at room temperature with a periodicity of approximately 2.2 nm and an order–disorder transition takes place at approximately 150 °C. The transition is reversible upon cooling/heating cycles. Implicitly, the materials are melt processable due to the fluid state in the disordered state.

Major recent efforts concern control of regioregularity, as it has profound effects on the structure and charge carrier mobility [284–301]. Self-assembly of poly(3-hexylthiophene)s results in a lamellar structure on SiO_2/Si substrates and relatively high charge carrier mobility of approximately $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was achieved using highly regioregular polymers and processing conditions that lead to the parallel alignment of the lamellae relative to the substrates (Fig. 3.17) [301]. This suggests high mobilities based on two-dimensional transport within self-assembled conjugated lamellae, which could be important for applications for polymer transistors within logic circuits and active-matrix displays. The selection of solvents [290, 298] and alkyl side-chain lengths is important for enhanced transport [299]: The average hole mobility varies from $1.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in poly(3-butylthiophene) and $1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in poly(3-hexylthiophene) to $2.4 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in poly(3-dodecylthiophene). Therefore, the hexyl side-chain seems to be optimal for charge transport. As already pointed out, self-assembly generally leads only to local order. This was clearly manifested in STM studies using regioregular poly(3-hexylthiophenes) on graphite, which demonstrated “folds” of the chains and differently aligned self-assembled domains [291–293].

The polyalkylthiophenes can be doped for conductivity. Regioregular poly(3-alkylthiophene)s have been p-doped with I_2 vapor and they display high room

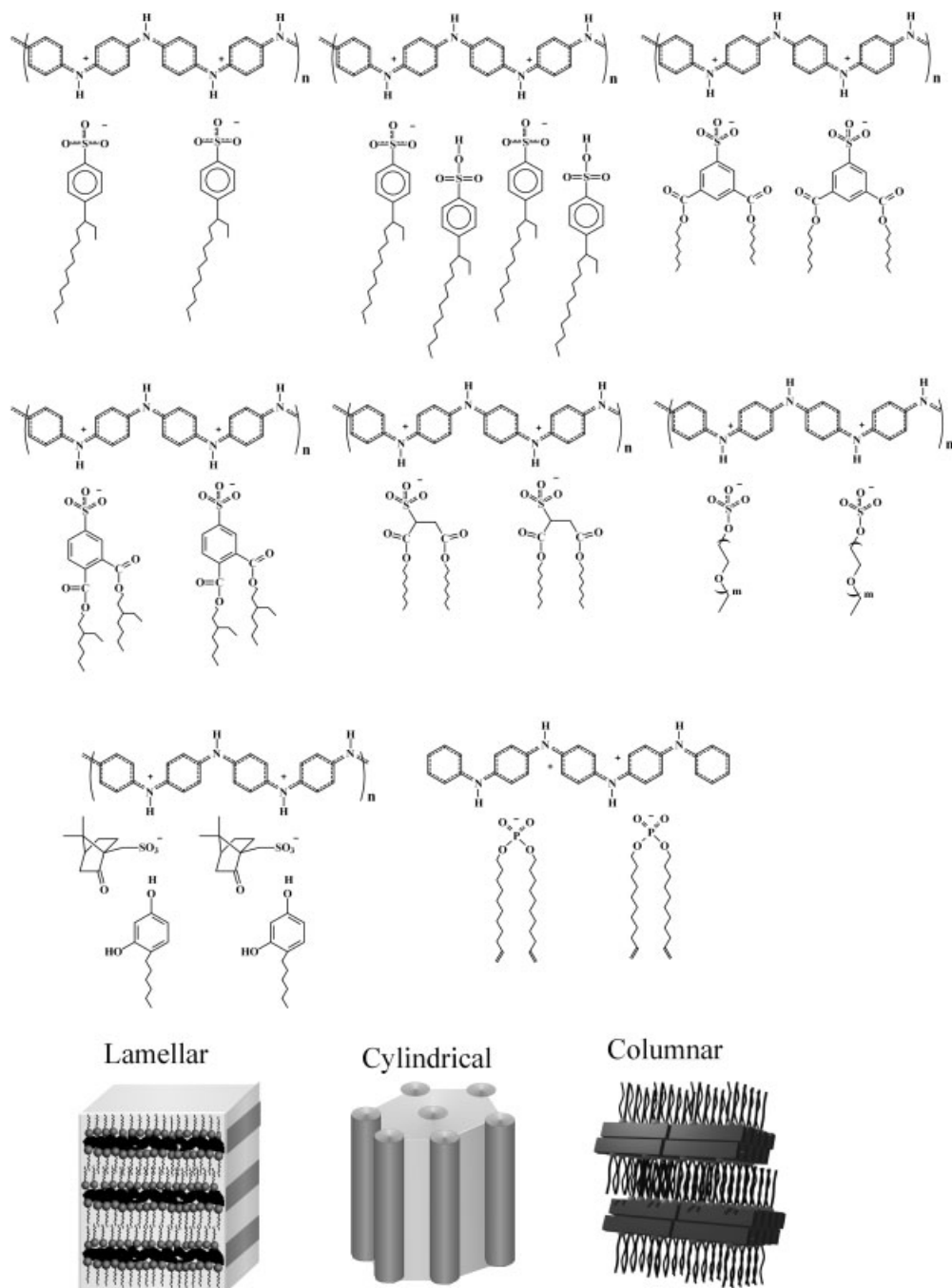


Fig. 3.18 Various acid doped complexes for polyaniline and oligomeric anilines [58, 82, 102, 175, 321, 324–330, 332, 333].

temperature conductivity ($100\text{--}750\text{ S cm}^{-1}$) [285, 286]. Langmuir–Blodgett techniques allow films with conductivity of $67\text{--}100\text{ S cm}^{-1}$ for the head-to-tail poly(3-hexylthiophene)–stearic acid compounds [287]. The side-chains allow tuning of the functionalities; one can also prepare “Janus-type” polythiophenes that have both hydrophobic alkyl side-chains and hydrophilic oligo(oxyethylene) side-chains [302]. They allow self-assembled monolayers on surfaces using Langmuir–Blodgett techniques. The side-chains can also be semifluorinated [303]. Side-chains have been connected to a wide variety of different polymers to allow hairy rods or comb-shaped polymers, self-assembly and tunable properties; for conjugated polymers see [100, 262, 271, 275, 304, 305] and for flexible polymers [17, 306]. Polyfluorenes with different alkyl chains are among the most feasible conjugated polymers for light-emitting devices and they also undergo self-assembly [307–312]. Comb-shaped regioregular poly(4-alkylquinoline-2,6-diyl)s show lamellar structures and π -stacking and emit yellow light at $542\text{--}557\text{ nm}$ [313]. Finally, it is pointed that the planarity can be controlled by supramolecules interactions [314, 315].

In the previous examples, the self-assembly is achieved based on the covalently connected repulsive side-chains. Self-assembly can also be achieved given that there exists a sufficiently strong physical attractive interaction to balance the repulsive interaction. Polyaniline is probably the most studied conjugated polymer in this context. The undoped state of polyaniline consists of benzenediamine and quinonediimine moieties [100, 316–318]. It can be doped by a redox reaction by electron transfer but, importantly, its salts with strong acids are electronically conducting due to protonation of the iminic nitrogen and a subsequent redox reaction along the chain [316, 319]. Note, however, that even earlier conducting polyaniline sulfate had been used in electrochemical applications [320]. An important finding was that the dopant can also have another functional group besides the protonating acid group [321]: It can contain, for example, alkyl spacers to reduce aggregation, it can contain surface-active groups for compatibilization, hydrogen-bonding sites, mesogens or dyes. A widely used functional counterion is dodecylbenzenesulfonic acid (DBSA) (Fig. 3.18). The bonding is due to ionic interaction and therefore the material can also be classified as a polyelectrolyte–surfactant complex. The stoichiometric complex where only the iminic nitrogens are protonated leads to infusible and solid crystalline material [322]. Adding more DBSA, i.e. using one DBSA molecule corresponding to each repeat unit of polyaniline, does not lead to phase separation, obviously as the additional molecules are bonded by hydrogen bonding to the sulfonates and amines. Such a composition leads to lamellar fluid-like self-assembly (Fig. 3.18) [58].

The counterion engineering allows one to tailor a balance between the conductivity and processability. The concept allows solid films using common solvents with conductivities as high as approximately $200\text{--}400\text{ S cm}^{-1}$ [321]. For example, using octanesulfonic acid [321] the solubility in low-polarity solvents may be reduced. However, the conductivity can simultaneously be increased for shorter side-chains, obviously due to a larger hopping conductivity between the

chains [323]. Upon increasing the total number of methyl groups in the side-chains, such as in dinonylnaphthalenesulfonic acid, the complexes become highly soluble in several solvents, but the conductivity is strongly reduced [324]. The effect of adding two alkyl chains with different lengths and different branchings has been systematically studied (Fig. 3.18) [102, 325–328]. The self-assembly, transport and other properties can also be tuned by additional amphiphilic compounds due to attractive and repulsive interactions. In this case the problem is to identify compounds that have sufficiently strong attractive interaction to the protonated main chain [82, 329, 330]. The phase behavior of supramolecular hairy rods has been studied theoretically [331]. The functionalized counterions allow even more complex structural tuning: self-assembly within colloidal suspensions can be used to template networks of electrically conducting sulfonic acid-doped polyaniline (see Fig. 3.9) [216].

The previous examples concern a comb-shaped architecture where the side-groups are either covalently or physically connected and which leads to self-assembly, given that the side groups are sufficiently long and repulsive. Next we address the linear architecture where the polymeric blocks are connected end-to-end. In an effort to combine electronic conductivity, there have already been early efforts to combine charge-transfer salts selectively within block copolymeric self-assembled domains. Polybutadiene-*b*-polyvinylpyridine block copolymer was complexed using 7,7',8,8'-tetracyanoquinodimethane [334, 335]. Self-assembled morphologies were obtained with conductivities of 10^{-3} – 10^{-4} S cm $^{-1}$. Mixed ionic and electronic conductors were prepared [336–338], for example by using poly(2,5,8,11,14,17,20,23-octaoxapentacosyl methacrylate)-*b*-poly(4-vinylpyridine) where LiClO $_4$ was added to the oxyethylene phase to obtain ionic conductors with conductivities of approximately 5×10^{-6} S cm $^{-1}$ and the 4-vinylpyridine phase was complexed with 7,7',8,8'-tetracyanoquinodimethane to obtain electronic conductivities of approximately 10^{-6} S cm $^{-1}$ at 25 C [336].

Examples have been shown here of how substitution of polythiophenes using short alkyl chains render solubility and self-assembly. Instead of the comb-shaped architecture, one could consider also the linear block copolymeric architecture where the solubilizing groups are at the ends. Well-defined triblock copolymers consisting of narrow molecular weight polystyrene end-groups of 30 repeat units and a central block of 11 thiophene groups form micelles of diameters of 12 nm in chloroform solution and in the solid state, consisting of a thiophene core (Fig. 3.19) [339]. Regioregular polyalkylthiophenes can also be used as blocks in block copolymers. Polystyrene-*b*-poly(3-hexylthiophene), polystyrene-*b*-poly(3-hexylthiophene)-*b*-polystyrene and poly(methyl acrylate)-*b*-poly(3-hexylthiophene)-*b*-polystyrene block copolymers have been studied, each having a narrow molecular weight distribution (Fig. 3.19) [340]. Nanoscale fibrillar morphology is obtained owing to aggregation of the conjugated domains due to stacking. I $_2$ doping renders conductivities that range from 4.6×10^{-5} to 110 S cm $^{-1}$. Based on atom-transfer radical polymerization (ATRP), poly(3-hexylthiophene)-*b*-polystyrene diblock copolymer with a polystyrene majority phase has been synthesized [341]. Nanoscale ribbons are observed where poly(3-hex-

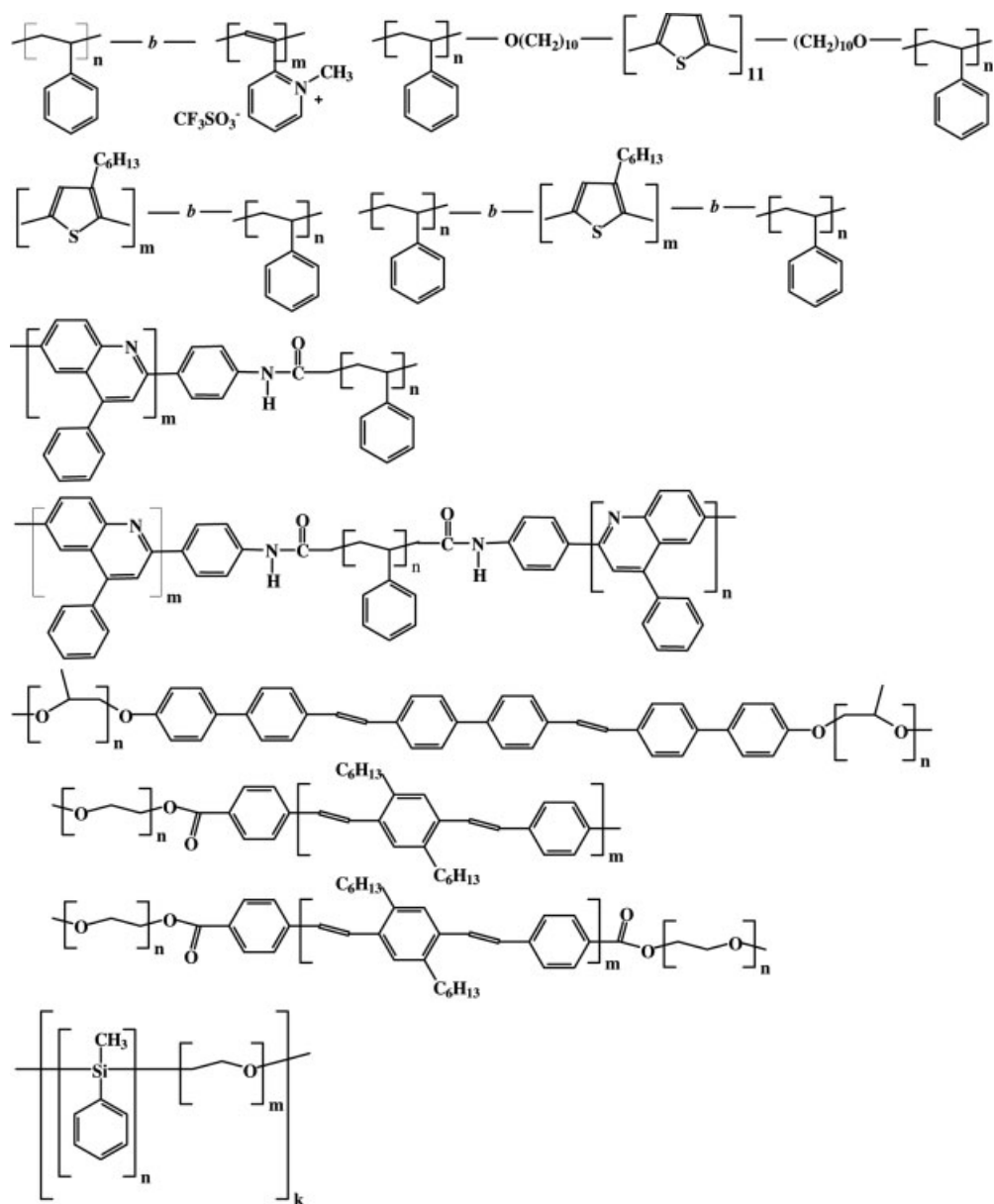


Fig. 3.19 Examples of block copolymers containing conjugated blocks [339–343, 345–349].

ylthiophenes) form the cores of the self-assembled ribbon-like entities. The structure is sensitive to selection of the solvents, which drastically reflects in the conductivity. I_2 doping leads to conductivity of the order $10^{-2} \text{ S cm}^{-1}$ but it is reduced if the ribbon-like morphology is not obtained. Aggregates of amphiphilic diblock copolymers based on styrene and thiophene were prepared by injection of polymer solution into water and by electrochemically induced formation of vesicles [342].

A low molecular weight diblock copolymer consisting of flexible polystyrene block and pyridinium trifluoromethanesulfonate-substituted polyacetylene has been synthesized (Fig. 3.19) [343]. Conductivity suggests an alternating insulator–semiconductor layered structure of the deposited films. A comprehensive discussion on functionalization of polyacetylene by functional pendant groups has been presented recently [344]. They show various functional properties such as liquid crystallinity, photoconductivity, light emission, photoresistance, chromism, helical chirality, optical nonlinearity, self-assembly, cytocompatibility and bioactivity.

Amphiphilic rod–coil diblock and coil–rod–coil triblock copolymers of oligo-(phenylenevinylene)-*b*-poly(ethylene glycol) and poly(ethylene glycol)-*b*-oligo-(phenylenevinylene)-*b*-poly(ethylene glycol) self-assemble into long cylindrical micelles [350]. The micelles have diameters of approximately 8–10 nm and are composed of an conjugated block surrounded by a poly(ethylene glycol) corona. An even more rigid conjugated block was used in triblock copolymers where the central block consists of three biphenyls connected using vinylene groups and the end blocks are poly(propylene oxide) [349]. A brilliant blue emission was observed with a fluorescence maximum at 479 nm. The molecules self-assemble into successively one-dimensional lamellar, two-dimension hexagonal and three-dimension tetragonal structures with increasing coil-to-rod volume fraction (Fig. 3.20).

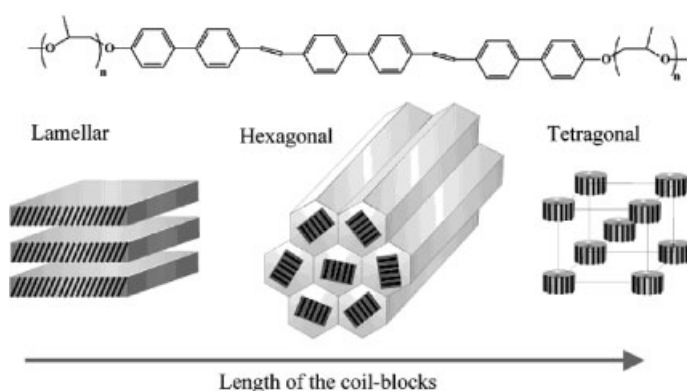


Fig. 3.20 An example of ABA-type coil–rod–coil triblock copolymer with a conjugated central block and the structures obtained [349].

Poly(phenylquinoline)-*b*-polystyrene rod-coil block copolymers have been extensively studied [346, 351]. They can self-assemble into hollow spherical micelles having diameters of a few micrometers. Including the third block, i.e. polyquinoline-NHCO-polystyrene-NHCO-polyquinoline rod-coil-rod triblock copolymer, spherical vesicles in solution are formed [347].

The structures of block copolymers consisting of various conjugated blocks and coiled blocks in thin films have recently been reported [352, 353]. The conjugated blocks are side-group modified polyphenylene, poly(phenyleneethynylene), polyfluorene or polyindenofluorene and the coiled blocks are polydimethylsiloxane, PEO or polystyrene [352, 353]. The copolymers organize as ribbons with constant width and height in the nanometer range (Fig. 3.21). The comparison of the experimental data with the theoretical modeling indicates that the ribbons are made of regular stacks of conjugated chains surrounded by coiled non-conjugated segments. In addition to π -conjugated polymers, δ -conjugated polymers allow self-assembly and interesting properties. An amphiphilic multi-block copolymer consisting of alternating PEO segments and polydisperse polymethylphenylsilane segments self-assemble as vesicles, micellar rods and helices in water-based solvents, even if the polymethylphenylsilane blocks have large polydispersity [348].

Dendronic side-groups in polymers allow detailed control of self-assembly [354–356]. Organic donor or acceptor groups can be connected to the apexes of the dendrons (Fig. 3.22). By selecting a polymer with complementary electron acceptor or donor groups as side-groups, electron-donor stacks can be formed within self-assembled columns that lead to enhanced charge carrier mobilities [355]. Conjugated dendritic thiophene derivatives have also been studied [357].

Finally, polymeric self-assembly can be used as a template to grow inorganic and metallic structures based on selective complexation of metal salts within block copolymer domains and consequent reduction (e.g. [358–363]). These and other deposition concepts can be applied to self-assembled structures to achieve conductivity [364]. Diblock copolymers consisting of dendritic bulky and flexible

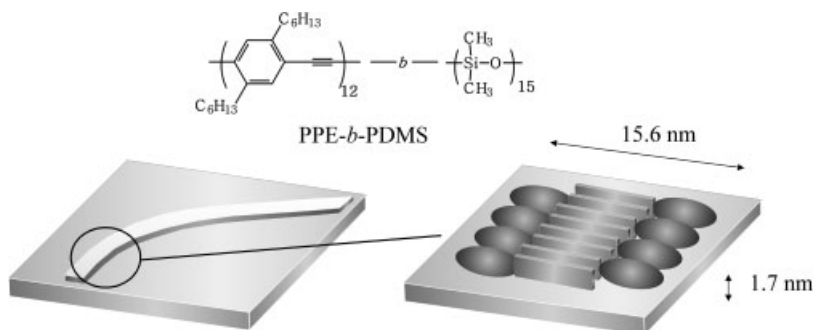


Fig. 3.21 Scheme of nanoscale ribbons based on hexyl-substituted polyphenyleneethynylene-*b*-polydimethylsiloxane block copolymer in thin films [352, 353].

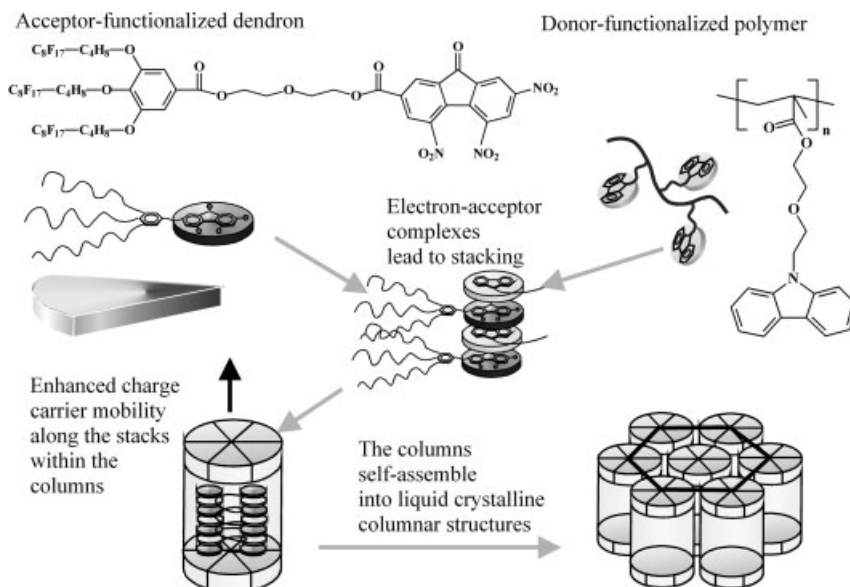


Fig. 3.22 An example of how electron acceptor and donors can be stacked within self-assembled domains for enhanced charge carrier mobility [355].

nonpolar carbosilane block and rigid helical polyisocyanide blocks form complexes with silver ions and lead to nanowires [365]. Distinct nanowires can be achieved by using polystyrene-*b*-poly(4-vinylpyridine) where pentadecylphenol is hydrogen bonded to the pyridines, which leads to hierarchical self-assembly [366]: Polystyrene cylinders within poly(4-vinylpyridine)-pentadecylphenol can be obtained and, after aligning and removing the pentadecylphenol, distinct polystyrene wires with a poly(4-vinylpyridine) corona are obtained [86, 109, 367], which can be metallized with CdSe, Pd, Ag and Au [368, 369]. The self-assembled domains of symmetrical polystyrene-*b*-poly(4-vinylpyridine) diblock copolymers have been used as templates to prepare Ag layers by electroless deposition and anisotropic conductivity was achieved along the lamellae [370]. Just in passing, we point out that self-assembling amyloid protein fibers, polyelectrolyte chains and even DNA can be used to construct nanowire elements [12, 371].

3.4

Optical Properties of Self-assembled Polymer Systems

As there exists a vast literature on the optical properties of polymers, such as on materials for light-emitting devices, electrochromism, liquid crystallinity, optical switching, photorefractive applications, photovoltaics and photoconductivity, we limit the present discussion to three topics which have an intimate connec-

tion with self-assembly, i.e. photonic crystals or bandgap materials, nonlinear optical materials and photovoltaic materials.

Well-defined dielectric structures at the optical length scale are able to manipulate flow of light [372–378]. This has attracted much attention over recent years in the context of optical communication, sensing, optical limiting and even coatings. Photonic crystals are long-range ordered structures whose refractive index varies in a spatially periodic manner. Taken that the periodicity matches the optical wavelengths, that the structure has proper symmetry and that sufficient dielectric contrast exists, the resulting photonic crystals may exhibit a forbidden bandgap where no photons are allowed to propagate. In combination with controlled defect structures, a wealth of applications in photonics are expected, e.g. capability to confine, guide and control light. If optical wavelengths are aimed for, the required periodicity is in the range 100–200 nm. Detailed structures and defects with sufficient dielectric contrast can be constructed using lithographic and etching techniques. For certain large area applications, simpler techniques could be more suitable. Spontaneous self-assembly of colloids [375], synthetic opals [379–384], inverted opals [379, 385–387] and block copolymers [218, 219, 221, 378, 388–402], on the other hand, allows the preparation of small enough structures. Although self-assembly leads to a well-defined local order and offers a potentially low-cost method for the production of photonic crystals, it is non-trivial to achieve perfectly ordered structures over the macroscopic length scale combining carefully engineered defects.

The simplest periodic dielectric structures capable of interacting with optical waves are dielectric mirrors, quarter-wave stacks or 1D photonic crystals which consist of alternating layers of high and low refractive index materials [218, 219, 221, 374, 388, 390, 392, 395, 397, 403]. It is a challenge to achieve high periodicity in the range 100–200 nm using purely block copolymers, as very high molecular weight polymers would be needed. High molecular weight usually leads to very slow achievement of the equilibrium structure during annealing and therefore it is challenging to obtain good enough overall order. In this respect, it can be helpful to construct the self-assembly using block copolymers with smaller molecular weights but where additionally homopolymers, oligomeric plasticizers or physically bonded amphiphiles or liquid crystals are added to the domains [218, 219, 221, 388, 390–392, 395, 397, 403] (Fig. 3.23). The blocks can also consist of rigid mesogenic moieties [395]. Roll casting [399] or various annealing procedures promote sufficient macroscopic order. Another critical aspect is the dielectric contrast. Most organic polymers have their refractive index in a narrow range around $n \approx 1.5$. Therefore, the dielectric contrast tends to remain small, but still allowing some bandgap effects. In order to increase the dielectric contrast, nanoparticles have been selectively sequestered to the structures [392, 397, 404]. For example, Au nanoparticles with polystyrene brushes are confined within the polystyrene layers of the self-assembled structures of polystyrene-*b*-poly(ethylene/propylene), C₁₈H₃₇-functionalized Au nanoparticles are confined in the interfaces and methyl-functionalized SiO₂ particles in the poly(ethylene/propylene) domains. In this way, the contrast can be increased. There have been

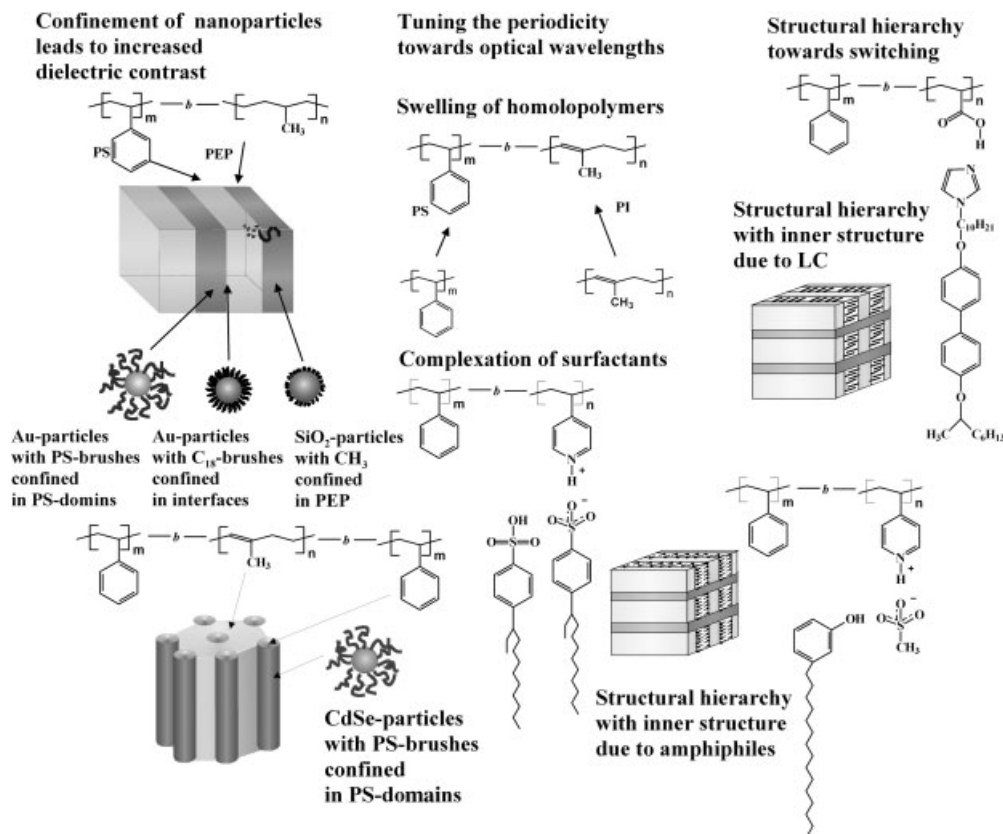


Fig. 3.23 Examples of block copolymeric systems aimed at photonic bandgap materials [218, 221, 378, 392, 395, 397].

recent efforts to achieve controllable and switchable photonic bandgap structures where abrupt color changes have been obtained upon heating and cooling due to phase transitions within the self-assembled structures [221, 395]. Such concepts might pave the way also towards smart coatings. In the purely layered geometry, it is not possible to achieve a complete photonic bandgap, which would stop the light propagation in all directions. Therefore, higher dimensional block copolymer structures have been pursued [374, 377, 393, 398, 400, 402]. Even 2D materials consisting of self-assembled cylinders do not allow a complete bandgap [399] and in this respect 3D network-like structures are currently being studied in detail [402]. An interesting concept, although not directly related to self-assembly, concerns the preparation of photonic crystals using holographic lithography [401].

As another example, optically nonlinear materials are discussed. Over the years, there have been considerable efforts to construct optically nonlinear polymer-based materials for novel optoelectronic devices (for reviews, see [405–409]).

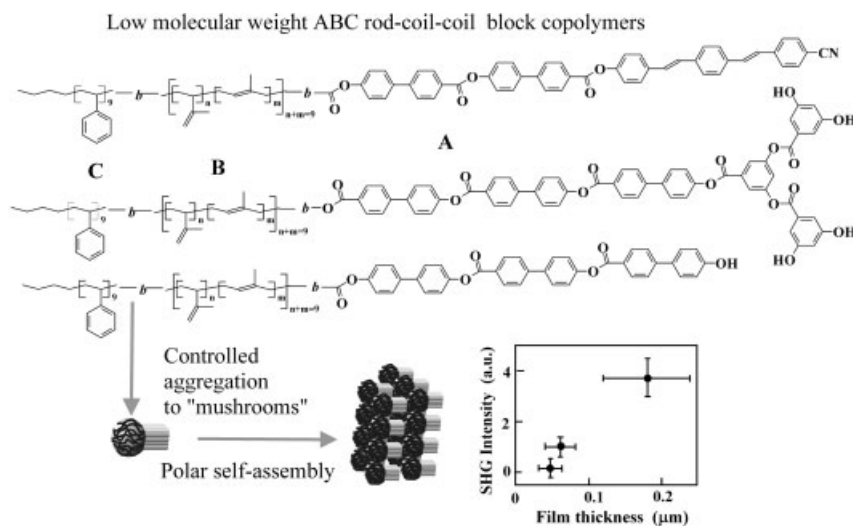


Fig. 3.24 Oligomeric rod-coil-coil triblock copolymers, which form “mushroom-like” structures and noncentrosymmetric self-assembly [419–428]. The materials show second-order harmonic generation (SHG) [419].

In particular, second-order nonlinear optical materials can double the frequency of the incident light and allow, for example, electro-optic modulators and laser frequency doublers. Such materials can be accomplished using chromophores which consist of electron acceptor and electron donor groups that are connected using a conjugated linker, given that the chromophores form noncentrosymmetric, i.e. polar, structures. Noncentrosymmetric structures are challenging to obtain and require specific materials and processes. Common techniques include alignment of the chromophores embedded in a polymeric matrix by an electric field, i.e. poling, and the subsequent “freezing” of their alignment by, for example, cooling the system to a glassy state, chemically immobilizing the chromophores by cross-linking or controlled deposition of the poled layers by Langmuir–Blodgett techniques [405–409]. Importantly, the poled chromophores are prone to relaxation towards the thermodynamic nonpolar equilibrium state, which can be a serious limitation considering the applications. In an effort to control the relaxation of the chromophore alignment, they have been covalently bonded to rigid rod polymers that undergo lamellar self-assembly [410–413]. Given that the system is poled before the self-assembly is frozen, the relaxation can be effectively suppressed to be only two-dimensional within the self-assembled lamellar layers.

There have been efforts to find concepts that would lead directly to a spontaneous equilibrium noncentrosymmetric assembly [33, 414–417]. Note that collagen possesses a relatively strong second-order nonlinear susceptibility [418]. In the present context, low molecular weight triblock copolymers consisting of a

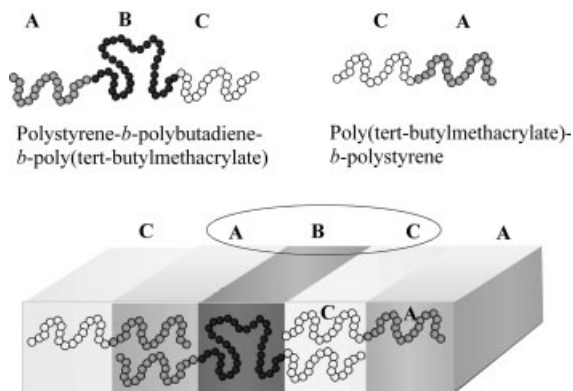


Fig. 3.25 Schematics for obtaining noncentrosymmetric self-assembly by mixing an ABC triblock copolymer and an AC diblock copolymer [430].

rod-like end block, flexible polyisoprene middle block and flexible but more bulky polystyrene end block are interesting (Fig. 3.24) [419–428]. The rods tend to aggregate mutually, but as the coils take up a larger lateral space, the packing becomes hindered. Therefore, a concurrent stretching of the coils takes place and the number of aggregated chains becomes controlled, e.g. approximately 100. This concept leads to mushroom-shaped supramolecular amphiphiles. They are reported to self-assemble curiously in monolayers in a noncentrosymmetric fashion [419–428]. As the rods can be functionalized, the concept offers spontaneous noncentrosymmetric self-assembly and second-order nonlinear optical properties (Fig. 3.24) [419, 426, 427], and also piezoelectricity [429]. Dendron-functionalized rod-coil-coil triblock oligomers can also bind nanocrystals and promote ultraviolet lasing [428].

Noncentrosymmetric self-assembly can also be obtained using mixtures of block copolymers. If one uses pure ABC triblock copolymers or pure AC diblock copolymers, the structures are symmetric. However, upon mixing ABC and AC block copolymers, macroscopic phase separation does not necessarily take place and the polymers can form noncentrosymmetric self-assembly within the mixtures, as shown schematically in Fig. 3.25 [430]. This concept can pave the way for various new functionalities.

The final example concerns polymeric photovoltaics (for recent reviews, see [431–435]) where block copolymeric self-assembly turns out to be interesting due to the enhanced amount of available interfaces [436–445].

In order to achieve a photovoltaic effect, charge generation to electrons and holes has to take place upon illumination. The electron-hole pair, or exciton, is strongly bound as the dielectric constant of organic matter is low. It is critical to collect the electrons and holes separately to the opposite current collectors, so avoiding recombination. This can be accomplished using domains of electron-accepting and electron-donating materials. If the exciton is created sufficiently

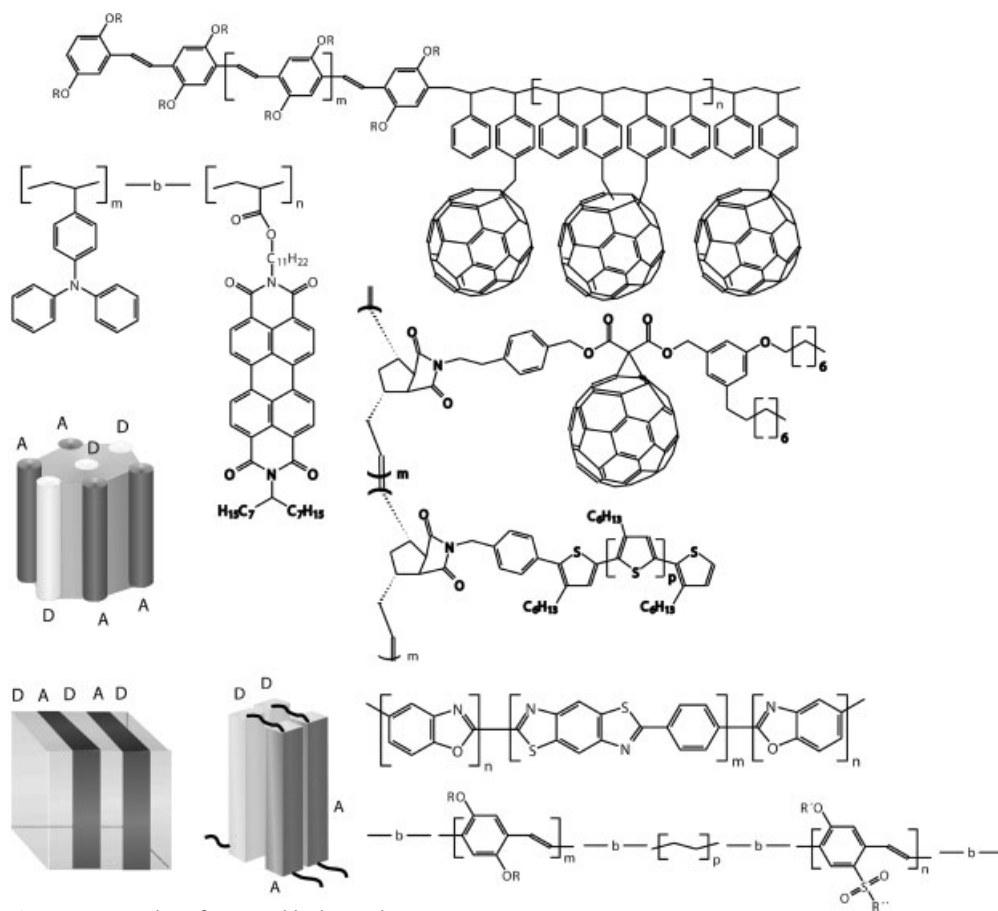


Fig. 3.26 Examples of various block copolymers containing electron-accepting (A) groups and electron-donating groups (D), and schemes for self-assembly that can lead to enhanced photovoltaic properties for charge collection to the external electrodes [436, 439, 444, 446].

close to such interfaces (less than approximately 10 nm), the exciton can be dissociated so that the electrons enter the electron-accepting material and the holes the electron-donating material. By applying an electric field and given that sufficient charge carrier diffusion exists within the two domain, the charges can be collected to the external collectors. There have been a variety of different routes to allow a high interfacial area between electron-acceptor and -donor materials, such as interpenetrating networks. Self-assembly could offer a feasible route, if also the alignment of the domains could be controlled. An ABA triblock conjugated copolymer, poly(2,5-benzoxazole)-*b*-poly(benzobisthiazole-2,6-diyl-1,4-phenylene)-*b*-poly(2,5-benzoxazole), shows self-assembly and efficient energy transfer [345]. A diblock copolymer consisting of alkoxy-substituted poly(*p*-phenylene-

vinylene) (PPV) and fullerene-functionalized polystyrene block has been described (Fig. 3.26) [436–438]. There the PPV blocks act as electron donors and the fullerenes are electron acceptors. Photophysical measurements show that there is efficient electron transfer from the excited PPV blocks to the fullerenes [436]. Multiblock copolymers consisting of electron-accepting alkoxy-substituted poly(*p*-phenylenevinylene) and electron-donating alkylsulfone-containing poly(*p*-phenylenevinylene) with alkyl bridging groups have been studied (Fig. 3.26) [439, 440]. The authors also considered feasible self-assemblies to enhance the charge carrier collection to the external electrodes. Poly(vinyltriphenylamine)-*b*-poly(triphenyl-1,3,5-triazine) self-assembles to allow hole-conducting moieties in the first domains and electron-conducting moieties in the latter domains [443]. Another variant consists of similar hole-conducting blocks but the electron-conducting domains contain perylene-3,4:9,10-tetracarboxylic moieties [446]. Transmission electron microscopy shows self-assembly, although a number of defects can be observed. Finally, diblock copolymers were recently synthesized containing poly(3-hexylthiophene) and fullerenes within the side-groups [444, 445].

3.5

Conclusion

We have discussed a few examples where self-assembled polymers and supramolecules are useful for tailoring properties for electrical and photonics applications. They allow the required periodic structures for photonic bandgap materials; they allow synergistic behavior for electrically conducting materials, as the conductivity and other properties can in principle be tailored separately; they allow processability of conjugated polymers by controlling the separation and packing between them, which is important for optical properties and electrical transport; and they allow noncentrosymmetric self-assembly, which leads to enhanced second-order nonlinear optical properties and piezoelectric behavior. In order to provide wide applications, especially on a larger scale, the economics is an important issue and there the recent achievements with living polymerization techniques may be relevant. Finally, beyond the self-assembly which leads to the local order, processing techniques have to be developed to control the overall order and to reduce the defects. Due to progress in these topics, self-assembled polymers are finding their way to applications.

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